ON THE DENSITY OF THE WATER VAPOUR.[1]

By Toshiaki SHIRAI.

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Introduction. On the molecular state of the water vapour many discussions were published. But they cannot be said decisive. Some[2] of them claim the existence of polymerised molecules such as $(H_2O)_n$ besides single molecules H_2O in the water vapour, while others[3] refute them. Most of these discussions are based on the data calculated indirectly, for example the density of the water vapour under the orthobaric state calculated from the vapour pressure and the heat of vaporization. In fact the data[4] of the density of the water vapour directly measured are so scarce that they are not sufficient to be used in this discussion. The data of Kornatz,[5] however, are somewhat sufficient, which were used by Bose[6] to conclude the existence of twice polymerized molecules $(H_2O)_2$ in equilibrium with single molecules. According to his formula we can obtain so much $(H_2O)_2$ molecules as to 8.9% at 100° under one atmosphere. But presisely examining his formula, it is found that it does not reproduce the data of Kornatz correctly. Therefore we must make more careful measurement of the density of the water vapour, which I have undertaken.

Experimental. The apparatus is shown in Fig. 1, which has been designed after that of Prof. Sameshima[5] with some modifications. A is a glass vessel, whose volume above the mark *b* is accurately measured filling mercury at several temperatures. The stopper of the vessel carries two pieses of platinum wire sealed in, to which is hanged a small glass bulb containing an accurately weighed sample. The small glass bulb is wound round by fine platinum wire as shown in the separate figure. Through this wire electric current is passed to break the bulb in order to set free the water vapour into vessel A. The vessel A is immersed in a thermostat, the temperature of which is kept constant within one tenth degree $\left(\text{or } \pm\frac{1}{20}^\circ\right)$.

(1) Translation of a paper published in the *Journal of the Chemical Society of Japan* (in Japanese), **44** (1923), 887.

(2) Winkelmann, *Wied. Ann.*, **9** (1880), 208; Oddo, *Gaz. chim. ital.*, **45** (1915), 319; Bose, *Z. Elektrochem.*, **14** (1908), 269; Weber, *Comm. Phys. Lab. Leiden*, No. 150.

(3) Kendall, *J. Am. Chem. Soc.*, **42** (1920), 2477; Menzies, *J. Am. Chem. Soc.*, **43** (1921), 851.

(4) Regnault, *J. de chim. et de phys.*, **15** (1845), 129; Horstmann, *Liebig's Ann. Chem., Sup. Bd.*, **6** (1868), 64; Kornatz, Inaug. Diss., Königsberg, 1908.

(5) Sameshima, *J. Am. Chem. Soc.*, **40** (1918), 1482.

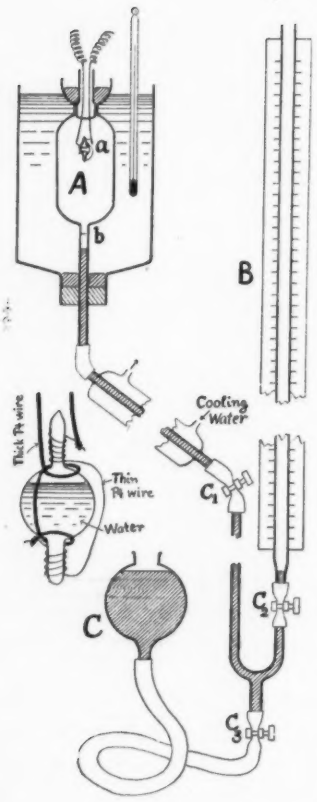

Fig. 1.

The liquid paraffine is used for the thermostat liquid, which is heated electrically. As the operating temperature lies so high as from 80° to 140°, the bath is carefully enveloped by thermal insulators, the electric current is continuously passed and only its small fraction is interrupted by means of a thermoregulator and a relay. The regulator is of ordinary type but the liquid filled is mercury only.

The measurement is carried out as follows. Raising the mercury reservoir C to fill the vessel A with mercury, we put the stopper fitted with the glass bulb already mentioned. Now lowering the reservoir, the vessel becomes to vacuum. This operation is repeated two or three times to get rid of any trace of gas occluded in the mercury or wall of the vessel. Adjusting the mercury level near the mark *b*, temperature of the thermostat is raised to the required temperature. Then adjusting the mercury level to the mark *b* accurately, the height of the mercury in the manometer B is noted. To make the change of the condition of the heated mercury column as small as possible, the connecting tube between A and B is covered with water jacket, and any moving of the heated part of mercury is avoided. For this purpose, in the case of breaking the glass bulb containing the sample, the connecting tube is shut at C_1 by means of a pinchcock. After the break, the counterbalancing mercury level in manometer B is aquired on several trials of slightly releasing the pinchcock at C_1.

The difference of the level in the manometer is reduced to the standard value with respect to temperature and gravity. This value (P) is the pressure exerted by the water vapour of w gr. The volume of the vapour V is that of the vessel subtracted by the net volume occupied by the glass of the sampling bulb, which always amounts to 0.03 c.c. And as the temperature of the bath (T) is known, we can calculate the apparent molecular weight (M) by the following equation

$$PV=\frac{w}{M}RT,$$

where $R=0.082068$ litre-atmosphere.

Following table contains the obtained value of M besides its percentage deviations from the ideal value 18.016. Here we find that no deviation exceeds one percent, and also in Fig. 2 it is shown that these deviations are of order comparable to that expected from the equation of state of water vapour. The lines in Fig. 2 represent the differences of the ideal density of water vapour and the densities calculated by means of van der Waals' equation

$$\left(P+\frac{a}{V^2}\right)(V-b)=rT,$$

where $a=0.01089$, $b=0.001362$[1], while the circlets represent the differences of the ideal density and the observed ones.

Temp. $T-273.09$	Volume of vapour (V) c.c.	Weight of water (w) gr.	Pressure (P) mm. Hg	Observed mol. wt. $M=\frac{wRT}{PV}$	Deviation from 18.016 (%)
80.03	312.28	0.04115	161.05	18.021	0.03
80.00	312.28	0.07188	280.3	18.085	0.38
100.03	306.07	0.03070	129.3	18.053	0.21
100.02	297.54	0.05170	226.4	18.060	0.24
99.99	306.07	0.08087	340.2	18.073	0.32
99.98	297.54	0.10050	435.2	18.060	0.24
100.00	311.68	0.12405	512.4	18.075	0.33
120.00	297.74	0.04959	226.4	18.037	0.12
120.03	297.74	0.10190	464.6	18.062	0.26
119.98	297.74	0.11160	508.7	18.064	0.27
119.99	297.74	0.11285	515.1	18.041	0.14
140.05	297.94	0.10730	513.2	18.083	0.37
140.00	297.94	0.11440	548.2	18.046	0.17
140.00	297.94	0.11623	556.8	18.052	0.20

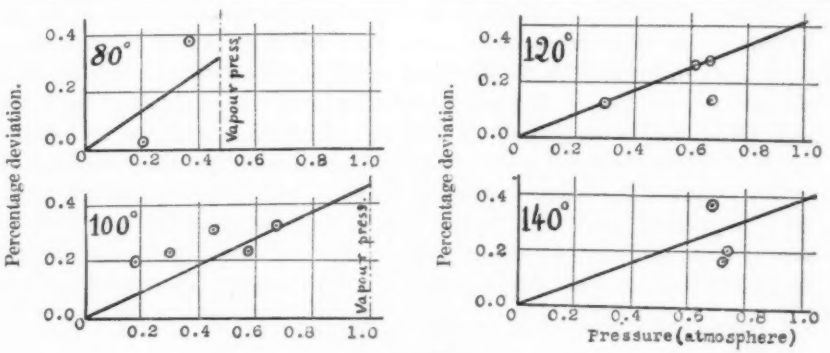

Fig. 2.

(1) Landolt-Börstein, "Tabellen," 4th ed., p. 447.

Occationally, however, irregularly higher values of deviation were obtained. In these cases either the vassel A was not clear or the quantity of water was too much that the pressure exerted by it was very near or exceeded the saturated vapour pressure at the temperature. Moreover, on strongly illuminating the vessel we could detect film glittering on the wall of the vessel. Therefore the higher deviation must be caused by such adsorption of water vapour on the stained wall. Now as to the higher deviations found in Kornatz's data, I do not know how to explain it, as I am not available of his original paper.

We can conclude, therefore, from the above measurements that the water vapour consists of single molecules only.

In conclusion the author wishes to express his best thanks to Prof. J. Sameshima for his kind guidance during the investigation.

March 1923.

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THE EFFECT OF ALKALI ON THE OXIDATION OF FERROUS HYDROXIDE WITH AIR.

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C. C. Palit and N. R. Dhar have found that some carbohydrates are oxydized by passing air through their solutions in the presence of ferrous hydroxide or sodium sulphite, and that the velocities of these induced oxidations increase with the increase of the concentration of caustic alkali almost in every case.(1) More or less similar results were obtained by Mittra and Dhar on the oxidation of nickelous hydroxide with air in the presence of ferrous hydroxide.(2) It may be supposed that the caustic alkali, which promotes the induced reaction is one of the substances which accelerate the primary reaction. In the case of ferrous hydroxide this expectation is more probable, for the reducing action of ferrous hydroxide increases as the concentration of alkali increases.(3) The present experiment has been

(1) **Palit and Dhar**, *J. Phys. Chem.*, **29** (1925), 799; **30** (1926). 939.
(2) **Mittra and Dhar**, *Z. anorg Chem.*, **122** (1922), 146.
(3) **Miyamoto**, *Japanese Journal of Chemistry*, **1** (1922), 57; *Scientific Papers of the Institute of Physical and Chemical Research*, **1** (1922), 31.

undertaken to know the effect of alkali on the primary reaction, for the purpose of knowing its effect on the induced reaction above described. From the result of the experiment, it has been ascertained that the caustic alkali does not promote the oxidation, but on the contrary, it decreases the velocity of oxidation. This is one of the examples which show the possibility of the existence of substances which do not promote the primary reaction but accelerate the induced reaction, and the mechanism of this phenomenon may be explained by the theory of the transference of active states.[1]

Experimental. A certain amount of ferrous sulphate solution of known concentration is added to a known quantity of sodium hydroxide solution of known concentration, and air, purified by passing through an acidic solution of potassium bichromate and sodium hydroxide solution, is passed at constant velocity into the mixture. The total volume of the mixture was made to 40 c.c. in each case. The concentration of sodium hydroxide given in the following tables are those calculated after the addition of ferrous sulphate solution. After t minutes the air current is stopped and the contents of the vessel are dissolved by adding sulphuric acid, and the ferrous sulphate thus formed is titrated with potassium permanganate solution (0.1018 normal), the volume of which is given as v in the following tables. The values of k in the following tables were obtained graphically, and those of $v_{calc.}$ were calculated by the equation, $v_{calc.}=v_0-kt$, v_0 being the value of v at $t=o$.

TABLE 1.

Temp.=20°C. Velocity of air=7.78 litres per hour. Concentration of alkali (C_{NaOH})=2.240 mol per litre. $k=0.140$ or $v_{calc.}=v_0-0.140\,t$.

t min.	v c.c.	$v_{calc.}$ c.c.	t min.	v c.c.	$v_{calc.}$ c.c.
0	9.11	—	0	12.60	—
6	8.10	8.27	6	11.50	11.76
8	8.00	7.99	8	11.32	11.48
10	7.74	7.71	10	11.18	11.20
12	7.54	7.43	12	10.97	10.92
15	7.05	7.01	15	10.66	10.50
0	10.83	—	0	18.20	—
6	9.90	9.99	6	17.11	17.36
8	9.65	9.71	8	16.99	17.08
10	9.30	9.43	10	16.69	16.80
12	9.20	9.15	12	16.51	16.52
15	8.79	8.73	15	16.12	16.10

(4) Miyamoto, *Scientific Papers of the Institute of Physical and Chemical Research*, 4 (1923), 257.

From the above results we see that the velocity of oxidation of ferrous hydroxide with air is zero order with regard to the amount of ferrous hydroxide, or the amount of ferrous hydroxide oxidized is independent of the quantity of hydroxide present. This can be explained by considering that the oxidation takes place in the liquid phase and not on the surface of the solid phase, because in liquid phase the concentration of ferrous ion, although it is extremely small, will be constant during the process.

The Effect of Alkali. Table 2 shows the results of the measurements which were carried out in the sodium hydroxide solution of different concentrations. The values of k decrease with the increase of the concentration of the alkali.

TABLE 2.

Temp. = 20°C. Velocity of air = 7.78 litres per hour.

C_{NaOH} mol/litre	t min.	v c.c.	$v_{calc.}$ c.c.		C_{NaOH} mol/litre	t min.	v c.c.	$v_{calc.}$ c.c.	
0.0048	0	9.11	—		0.870	0	9.06	—	
	6	7.10	7.25			6	7.54	7.68	
	8	6.76	6.63	$k=0.310$		8	7.15	7.22	$k=0.230$
	10	5.90	6.01			10	6.82	6.76	
	12	5.49	5.39			12	6.45	6.30	
	15	4.85	4.46			15	5.84	5.61	
0.0894	0	9.11	—		1.320	0	9.06	—	
	6	7.15	7.31			6	7.66	7.84	
	8	6.60	6.71	$k=0.300$		8	7.28	7.44	$k=0.203$
	10	5.93	6.11			10	7.10	7.03	
	12	5.61	5.51			12	6.69	6.62	
	15	4.85	4.61			15	6.20	6.01	
0.410	0	9.06	—		3.150	0	9.06	—	
	6	7.20	7.39			6	8.25	8.40	
	8	6.65	6.84	$k=0.278$		8	8.07	8.18	$k=0.110$
	10	6.41	6.28			10	7.97	7.96	
	12	5.65	5.72			12	7.76	7.74	
	15	5.06	4.89			15	7.58	7.41	

The Effect of Temperature. The results of the measurements at 30°C. and 40°C. are shown in Table 3. Thus the effect of temperature on the velocity of oxidation of ferrous hydroxide by the air is rather small.

TABLE 3.

Velocity of air = 7.78 litres per hour.

Temp. C°.	C_{NaOH} mol/litre	t min.	v c.c.	$v_{calc.}$ c.c.		Temp. C°.	C_{NaOH} mol/litre	t min.	v c.c.	$v_{calc.}$ c.c.	
30	2.240	0	9.05	—		40	2.240	0	9.02	—	
		6	7.96	8.09				6	7.88	7.92	
		8	7.71	7.77	$k=0.160$			8	7.50	7.55	$k=0.184$
		10	7.39	7.45				10	7.22	7.18	
		12	7.17	7.13				12	6.91	6.81	
		15	6.75	6.65				15	6.40	6.26	
30	0.870	0	9.05	—		40	0.870	0	9.02	—	
		6	7.50	7.64				6	7.38	7.54	
		8	7.03	7.17	$k=0.235$			8	7.09	7.04	$k=0.247$
		10	6.85	6.70				10	6.64	6.55	
		12	6.32	6.23				12	6.09	6.06	
		15	5.73	5.52				15	5.53	5.32	

$\frac{k_{30°}}{k_{20°}} = 1.14$ and $\frac{k_{40°}}{k_{30°}} = 1.15$ when $C_{NaOH} = 2.240$ mol/litre.

$\frac{k_{30°}}{k_{20°}} = 1.02$ and $\frac{k_{40°}}{k_{30°}} = 1.05$ when $C_{NaOH} = 0.870$ mol/litre.

The Effect of the Velocity of Air Current Passed. In the measurements above described, air was passed at the rate of 7.78 litres per hour. Table 4 shows the results obtained when the velocity of air current was changed. By comparing these values with those given in Table 1, it will be seen that the velocity of the oxidation increases slightly with the increase of the velocity of air current.

TABLE 4.

Temp. = 20°C. $C_{NaOH} = 2.240$ mol per litre.

Velocity of air litre/hour	t min.	v c.c.	$v_{calc.}$ c.c.		Velocity of air litre/hour	t min.	v c.c.	$v_{calc.}$ c.c.	
6.67	0	8.95	—		10.00	0	8.90	—	
	6	8.07	8.19			6	7.90	8.02	
	8	8.02	7.94	$k=0.126$		8	7.75	7.73	$k=0.146$
	10	7.71	7.69			10	7.52	7.44	
	12	7.39	7.44			12	7.24	7.15	
	15	7.12	7.06			15	6.90	6.71	

Summary.

The velocity of the oxidation of ferrous hydroxide with air was found to be independent of the quantity of ferrous hydroxide in a definite volume.

The effect of temperature on the reaction was small.

Caustic alkali does not promote the oxidation, and on the contrary, it decreases the velocity of oxidation, notwithstanding the reducing power of ferrous hydroxide increases with the increase of the concentration of alkali. From this result, we may suppose that the increase of the velocity of oxidation of carbohydrates or nickelous hydroxide by the addition of caustic alkali is not due to the increase of the velocity of primary reaction.

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ÜBER DAS GLEICHGEWICHT DES SYSTEMS GLUKOSE–KOCHSALZ–WASSER.

Von **Shinnosuke MATSUURA.**

Eingegangen am 8 Januar 1927. Ausgegeben am 28 Februar 1927.

Man findet in der chemischen Literatur verschiedene Verbindungen zwischen Glukose und Natriumchlorid,[1] so z. B. $(C_6H_{12}O_6)_2$ $NaCl{\cdot}H_2O$, $(C_6H_{12}O_6)_2$ $2NaCl{\cdot}H_2O$ und $(C_6H_{12}O_6){\cdot}2NaCl$, unter denen die erste, die von zwei Moleküle Glukose und einem Molekül Natriumchlorid gebildet ist, am sichersten bekannt ist, und schon im Jahre 1850 von Pasteur in diabetischem Harn aufgefunden wurde. Nach Städeler wird die zweite Verbindung, die durch die Vereinigung von je einem Molekül Glukose und Kochsalz gebildet ist, bei langsamem Verdunsten eines mit Natriumchlorid gesättigten, diabetischen Harns gewonnen. Was das Vorhandensein der dritten Verbindung anlangt, so ist es heute noch etwas zweifelhaft.

Die oben an erster Stelle genannte Verbindung $(C_6H_{12}O_6)_2$ $NaCl{\cdot}H_2O$ soll auch bei der Darstellung der Glukose gebildet werden, indem man Stärke mittels Salzsäure spaltet und nachher die so erhaltene saure Lösung mit Soda neutralisiert. Da die phasengesetzliche Untersuchung über das System Glukose-Kochsalz-Wasser, vom technisch-chemischen Standpunkt betrachtet, wichtig und interessant zu sein scheint, so habe ich diese in der vorliegenden Arbeit unternommen.

(1) Beilstein, "Handbuch der organischen Chemie," 3. Auflage (1893), I. S. 1046.

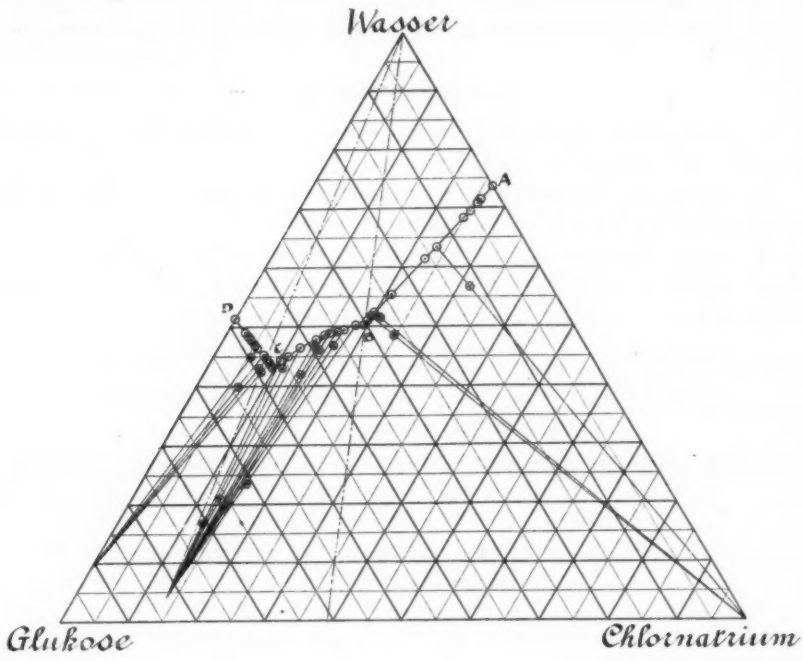
Beschreibung der Versuche. Die in dieser Untersuchung gebrauchte Glukose wurde von E. Merck und das Kochsalz von Kahlbaum bezogen. Die Glukose wurde vorher im Exsiccator auf Phosphorpentoxyd sorgfältig getrocknet.

Das Gemisch von Glukose-Kochsalz-Wasser wurde im Thermostat bei 24° etwa zwei Tage umgerührt und danach einige Stunden ruhig gelassen. Die klare Mutterlauge wurde alsdann herausgenommen und der Analyse unterworfen. Der Bodenkörper (mit etwas Lösung) wurde gleichfalls analysiert. Da ein an Glukose reicher Teill eicht die Erscheinung der Übersättigung zeigt, so musste man die Lösung mit einer Krystallsamen der Glukose impfen und einige Tage ruhig stehen lassen, bevor das Gleichgewicht zwischen fester und flüssiger Phasen vollständig hergestellt wurde.

Natriumchlorid wurde volumetrisch mit 1/10 N. Silbernitratlösung analysiert, indem man Kaliumchromatlösung als Indikator benutzte, und in dem Falle, wo eine grosse Menge der Glukose in der Lösung vorhanden war. noch einigen Tropfen der Salpetersäure dazu gefügt wurde. Die Glukose wurde folgedermassen bestimmt: Zur Glukose enthaltende Lösung wurde zuerst Schwefelsäure und dann Chromsäure zugefügt und dann erhitzt. Die dabei entweichenden Gase wurden zuerst durch ein mit Silbernitratlösung gefülltes Gefäss geleitet, um den beigemengte Chlorwasserstoff zu entfernen, und dann in eine 80 cm. lange, im vorderen Teil mit Kupferoxyd, und hinteren Teil mit einer Siberspirale versehene Verbrennungsrohr hineingeführt und verbrant. Nun wurde das Gas durch Trockenröhren mit konzentrierter Schwefelsäure und Calciumchlorid geleitet, schliesslich liess man das Kohlendioxyd, welches aus vollständiger Oxydation von Glukose resultierte, von der Kalilauge absorbieren. Die Glukosemenge wurde sodann aus dem Gewicht des Kohlendioxydes durch Rechnung festgestellt. Die Glukosemenge in die glukosereichen Teile wurden auch durch Polarimeter bestimmt. Die Kompositionsermitterung wurde anderseits dadurch bewerkstelligt, dass man Viskosität und spezifisches Gewicht der Lösung bestimmt, die durch Verdünnung der gesättigter Lösung oder durch Auflösung des Bodenkörpers (mit etwas Lösung) gewonnen werden, und die so erhaltenen Resultate in graphischer Darstellung bringt. In dieser Figur kann man die Komposition der gesättigten Lösung oder des Bodenkörpers (mit etwas Lösung) ablesen.

Die folgende Tabelle enthält die Komposition der gesättigten Lösung und des mit dieser im Gleichgewicht stehenden Bodenkörpers (mit etwas Lösung), welche in Gewichtprozent aufgestellt sind. Das graphische Dreieck wurde zeichnerisch nach Schreinemakers dargestellt.

Nummer	Lösung			Bodenkörper mit Lösung			Zusammensetzung der festen Phase aus Restanalysen ermittelt
	Glukose	Natrium-chlorid	Wasser	Glukose	Natrium-chlorid	Wasser	
1	0.00	26.48	73.52	—	—	—	
2	2.84	25.87	71.29	—	—	—	
3	3.58	25.58	70.84	—	—	—	
4	5.21	25.28	69.51	—	—	—	
5	6.82	24.85	68.33	—	—	—	
6	9.90	24.10	66.00	—	—	—	
7	13.09	23.38	63.53	11.70	31.52	56.78	NaCl
8	15.81	22.76	61.43	—	—	—	
9	19.77	21.90	58.33	—	—	—	
10	23.87	20.83	55.30	—	—	—	
11	27.81	19.87	52.32	27.39	21.06	51.55	„
12	28.35	19.85	51.80	26.57	24.86	48.57	„
13	29.47	19.50	51.03	—	—	—	NaCl + $[C_6H_{12}O_6]_2 \cdot NaCl \cdot H_2O$
14	31.70	18.10	50.20	60.74	15.71	23.55	$[C_6H_{12}O_6]_2NaClH_2O$
15	33.74	16.87	49.39	—	—	—	
16	33.76	16.84	49.40	36.59	16.59	46.82	„
17	34.92	15.98	49.10	66.35	14.45	19.20	„
18	35.98	15.12	48.90	38.00	15.00	47.00	„
19	36.90	14.50	48.60	43.69	14.39	41.92	„
20	38.67	13.61	47.72	39.61	13.40	46.99	„
21	41.62	11.92	46.46	66.28	12.70	21.02	„
22	44.05	10.95	45.00	46.02	11.00	42.98	„
23	45.60	10.24	44.16	70.79	12.31	16.90	„
24	47.35	9.57	43.08	—	—	—	$[C_6H_{12}O_6]_2NaCl \cdot H_2O + C_6H_{12}O_6 \cdot H_2O$
25	47.38	9.22	43.40	—	—	—	
26	47.35	8.45	44.20	49.49	8.21	42.30	$C_6H_{12}O_6 \cdot H_2O$
27	47.23	8.28	44.49	49.34	7.67	42.99	„
28	47.73	7.65	44.62	—	—	—	
29	47.55	7.20	45.25	54.06	6.02	39.92	„
30	47.74	6.97	45.29	—	—	—	
31	48.08	5.60	46.32	49.74	5.30	44.96	„
32	48.17	5.01	46.82	—	—	—	
33	48.12	4.04	47.84	—	—	—	
34	48.13	3.27	48.60	—	—	—	
35	48.55	2.49	48.96	—	—	—	
36	48.68	0.00	51.32	—	—	—	



Die Punkten auf den Kurvenanteil AB in der Figur (1–11 in der Tabelle) wurden folgendermassen erhalten : man bereitet vorerst die Glukoselösung mit bekannter Konzentration und zufügt dieser verschiedene Mengen von Natriumchlorid, wobei die Glukose immer in der Lösung gelöst bleibt, und das Bodenkörper nur von Natriumchlorid besteht. Infolgedessen kann man die Menge der Glukose, die jedem Punkt auf den Kurvenanteil A B entspricht, durch Rechnung bekommen, wenn man nur die Natriumchloridmenge analytisch erkennt.

Die Glukosereichenteile in den Punkten auf den Kurvenanteil C D haben Neigung eine übersättigte Lösung zu ergeben, und die Löslichkeit von Glukose ist daher schwer zu bestimmen.

In dieser Weise, habe ich also als feste Phase nur eine Verbindung $(C_6H_{12}O_6)_2NaCl{\cdot}H_2O$ bei 24° gefunden, welche in Rhomboeder auskrystallisiert. Wie man aus der graphischen Darstellung ersieht, zerfällt es beim Auflösen in Wasser. Fügt man dagegen Natriumchlorid dazu, wird diese Verbindung wieder abgeschieden, da ihre Löslichkeit dabei stark vermindert wird. Die Verbindung $(C_6H_{12}O_6)_2 2NaCl{\cdot}H_2O$, die Städeler beschrieb, kann ich nicht bei 24° auffinden. Wahrscheinlich mag diese ein Gemenge von $(C_6H_{12}O_6)_2NaCl{\cdot}H_2O$

und NaCl sein. Die Verbindung $(C_6H_{12}O_6)2NaCl$ mag auch ein Gemenge sein, welches bei der Verdunstung der Lösung im Punkt B zuletzt entsteht.

Zusammenfassung.

1. Das heterogene Gleichgewicht des Systems Glukose-Kochsalz-Wasser wurde bei 24° untersucht.

2. Zwischen Glukose und Natriumchlorid ist nur eine Verbindung $(C_6H_{12}O_6)_2NaCl{\cdot}H_2O$ bei 24° existenzfähig.

3. Diese Verbindung zersetzt sich bei Auflösen in Wasser. Durch Zusatz von Kochsalz zu der Lösung wird jedoch dieselbe Verbindung wieder auskrystallisiert, weil ihre Löslichkeit dadurch stark vermindert wird.

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SPECTROCHEMICAL STUDIES OF HYDROXYAZO-COMPOUNDS. PART III.[1]

By **Taku UEMURA, Naomichi YOKOJIMA** and **Tamimatsu ENDO.**

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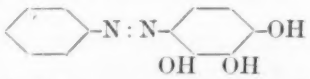
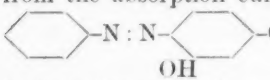
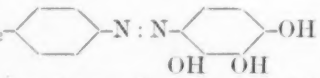
1. Benzeneazopyrogallol,[2] 

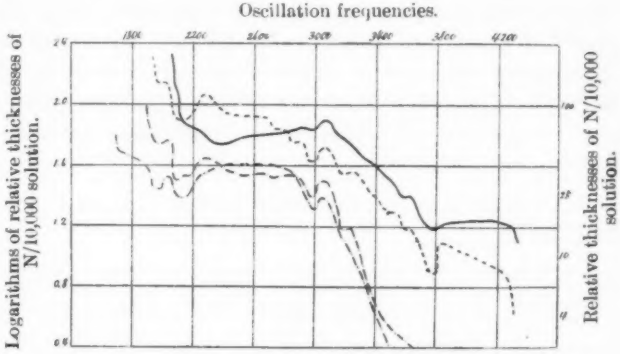
We can find very slight bathochromic and hyperchromic influences by the addition of alkali in the absorption curve (Fig. 1), and can hardly detect the change of colour in the solution. The marked difference from the absorption curves of No. 2 compound in Part I of this paper,  , is probably due to the existence of the meta hydroxyl-group with respect to the azo-group in this compound. We can assign A-form to the neutral state, but the alkaline state is perhaps the mixture of A- and R-forms.

2. p-Nitrobenzeneazopyrogallol,[3] 

KOH changes the colour of the solution from yellowish red into brown

(1) Part I and Part II of this paper were published in this journal, **1** (1926), 260 and **2** (1927), 10 respectively.
(2) Beilstein "Handbuch der Organischen Chemie," IV (1899), 1450.
(3) Obtained from p-nitraniline and pyrogallol.

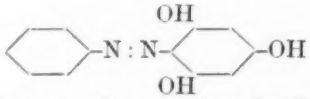
and soon into orange. A-form can be assigned to the neutral solution as usual, and R-form to the alkaline solution, but we think that on account of the meta hydroxyl with regard to the azo-group, B-form cannot be assigned in this case (Fig. 1).


Oscillation frequencies.
Logarithms of relative thicknesses of N/10,000 solution.
Relative thicknesses of N/10,000 solution.

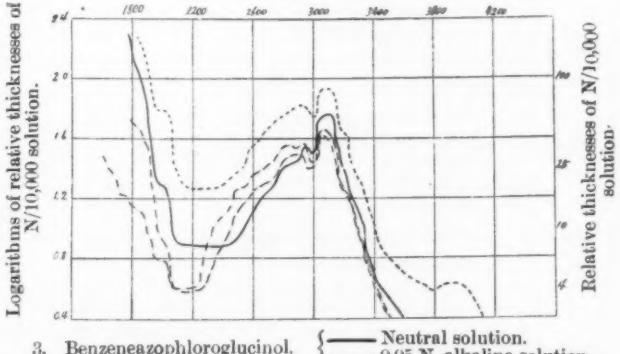
1. Benzeneazopyrogallol. { —— Neutral solution. - - - - 0.05 N. alkaline solution.
2. p-Nitrobenzeneazopyrogallol. { —·—· Neutral solution. —··—·· 0.0596 N. alkaline solution.

Fig. 1.

3. Benzeneazophloroglucinol,[1]



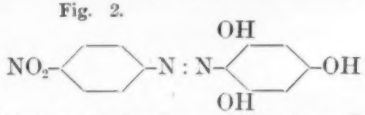
The yellow neutral solution does not change colour by the addition of potassium hydroxide solution. The hypochromic effect due to an alkali is rather exceptional (Fig. 2), but this is perhaps owing to a kind of destruction which has occurred in the molecule by the mutual hindrance of three movable hydrogen atoms in hydroxyl-groups.


Oscillation frequencies.
Logarithms of relative thicknesses of N/10,000 solution.
Relative thicknesses of N/10,000 solution.

3. Benzeneazophloroglucinol. { —— Neutral solution. - - - - 0.05 N. alkaline solution.
4. p-Nitrobenzeneazophloroglucinol. { —·—· Neutral solution. —··—·· 0.05 N. alkaline solution.

Fig. 2.

4. p-Nitrobenzeneazophloroglucinol,[2]



By the addition of an alkali, only a slightly bathochromic effect can be

(1) Obtained from aniline and phloroglucinol.
(2) Obtained from p-nitraniline and phloroglucinol.

seen in the absorption curve of this substance (Fig. 2), and this case, the yellowish red neutral solution changes into the orange red alkaline solution. Although we can give A- and R-forms to the two kinds of coloured solutions of this compound, it is almost safe to say that B-form is not represented owing to the mutual hindrance of labile hydrogen atoms.

All of the experimental results (Parts I, II, and III) may be summarized as follows:

No.		Compounds.	Colour of		Form to be assigned.
			Neutral solution.	Alkaline solution.	
Part I.	1	p-Hydroxyazobenzene.	y.	deep y.	A;R.
	2	Benzeneazoresorcinol.	y.	deep y.	A;R.
	3	Benzeneazo-p-cresol.	y.	r.	A;R.
	4	p-Nitrobenzeneazophenol.	y.r.	r.	A;R.
	5	p-Nitrobenzeneazoresorcinol.	r.y.	b.v.	A;R;B.
	6	m-Nitrobenzeneazoresorcinol.	y.	r.	A;R.
	7	p-Nitrobenzeneazo-p-cresol.	y.	v.	A;B.
Part II.	1	Benzeneazocatechol.	y.	o.	A;(A+R).
	2	Benzeneazoquinol.	light y.	nearly no change.	A.
	3	p-Nitrobenzeneazocatechol.	y.r.	b. (changeable).	A;B.
	4	p-Nitrobenzeneazoquinol.	y.r.	o. (changeable).	A;R.
	5	m-Nitrobenzeneazophenol.	y.	r.	A;R.
	6	o-Nitrobenzeneazophenol.	y.	r.	A;R.
	7	o-Nitrobenzeneazoresorcinol.	y.	r.	A;R.
	8	p-Nitrobenzeneazoguaiacol.	y.	r.	A;R.
	9	p-Nitrobenzeneazohydroquinone mono-methyl ether.	y.r.	p. (changeable).	A;R.
Part III.	1	Benzeneazopyrogallol.	y.	no change.	A;(A+R).
	2	p-Nitrobenzeneazopyrogallol.	y.r.	br. (changeable).	A;R.
	3	Benzeneazophloroglucinol.	y.	no change.	A.
	4	p-Nitrobenzeneazophloroglucinol.	y.r.	o.r.	A;R.

y. = yellow, r. = red, o. = orange, b. = blue, br. = brown, p. = purple, v. = violet.
y.r. = yellowish red, r.y. = reddish yellow, b.v. = bluish violet, o.r. = orange red.

Summary (Parts I, II, and III).

1. Tautomeric transpositions may take place in these hydroxyazo-compounds by the addition of a potassium hydroxide solution, with an accompanying change in colour.

2. We can respectively assign A(azo)-, R(red)-, and B(blue)-forms to these tautomers. (Sometimes we recognise more readily the mixture of these forms.)

3. Tautomerism is due to the labile hydrogen atoms in hydroxyl-groups which take the ortho- or para-position with respect to the azo-group.

4. The hydrogen atom which is in the meta hydroxyl-group with regard to the azo-group does not only move by itself, but moreover hinders the transposition of the other hydrogen atoms.

5. When there are many labile hydrogen atoms, mutual hindrance may occur.

6. B-form is sometimes produced only when there is a para nitroradical with regard to the azo-group.

7. Nitro-groups which take the ortho- or meta-position with respect to the azo-group do not change into the isonitro-structure.

8. The nitro-group has considerable bathochromic influence upon these hydroxyazo-compounds.

9. Generally only one absorption band exists in the solutions of these substances, but there are two bands when methyl-group is included.

The authors wish to express their hearty thanks to Prof. Yuji Shibata of the Tokyo Imperial University who offered them valuable advice in their researches.

The expenses of this study were defrayed partly through a grant from the Department of Education, and partly with the Research Fund of the School, for which we desire to tender our gratefulness.

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THE CONDENSATION OF PHENOLIC ALDEHYDES AND THEIR ETHERS WITH METHYL ETHYL KETONE.

By **Kenji IWAMOTO.**

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Harries and Müller[1] showed that, in the presence of an alkali, methyl ethyl ketone condenses with benzaldehyde to form the α-benzylidene derivative, $C_6H_5CH:CHCOC_2H_5$, and, in the presence of hydrochloric acid, to form the γ-benzylidene derivative, $C_6H_5CH:C(CH_3)COCH_3$. Ichikawa[2] reported that methyl ethyl ketone condenses with vanillin in the presence of an alkali, to yield 3-methoxy-4-hydroxystyryl ethyl ketone, $C_6H_3(OH)(OCH_3)CH:CHCOC_2H_5$, and, in the presence of hydrochloric acid, to give rise to the

(1) *Ber.*, **35** (1902), 966.

(2) *Sci. Rep. Tohoku. Imp. Univ.*, **14** (1925), 127.

bimolecular compound, $C_6H_3(OH)(OCH_3)CH:CHCOC(CH_3):CHC_6H_3(OH)(OCH_3)$. Claisen and Claperède[1] found that, in the presence of hydrochloric acid, benzaldehyde condenses with acetone to form dibenzylidene acetone, $C_6H_5CH:CHCOCH:CHC_6H_5$, and Nomura and Hotta[2] observed that divanillylidene acetone, $C_6H_3(OH)(OCH_3)CH:CHCOCH:CHC_6H_3(OH)(OCH_3)$, was formed by the condensation of vanillin with acetone in the presence of concentrated hydrochloric acid.

From these results, it appears that acetone condenses with benzaldehyde or with vanillin in the presence of hydrochloric acid, to form a bimolecular compound, arising from the condensation of two molecules of aldehyde and one of acetone, whilst, in the presence of hydrochloric acid, methyl ethyl ketone gives different condensation products, according as benzaldehyde or vanillin is condensed with it. Therefore, it seemed interesting to study the condensation of various phenolic aldehydes and their ethers with methyl ethyl ketone,—alkali, consentrated hydrochloric acid, or dry gaseous hydrogen chloride being used as the condensing agents.

The author condensed methyl ethyl ketone with protocatechualdehyde, veratraldehyde, piperonal, p-hydroxybenzaldehyde, anisaldehyde, m-hydroxybenzaldehyde, or with m-methoxybenzaldehyde under various conditions. The condensation may be represented by one of the following three cases :—

$$RCHO+CH_3COC_2H_5 \longrightarrow RCH:CHCOC_2H_5. \quad (A.)$$
$$RCHO+CH_3COC_2H_5 \longrightarrow RCH:C(CH_3)COCH_3. \quad (B.)$$
$$2RCHO+CH_3COC_2H_5 \longrightarrow RCH:CHCOC(CH_3):CHR. \quad (C.)$$

The constitution of the products (A) and (B) was determined by analysis, and by the formation of oxime and dibromide, and they were differentiated from each other by using sodium hypochlorite, when substance (B) yielded chloroform and an acid with one fewer carbon atom than the original ketone, as shown in the following scheme :—

$$RCH:C(CH_3)COCH_3+3NaClO=RCH:C(CH_3)COONa+CHCl_3+2NaOH.$$

The compounds which were expected to be, on analysis, of the type (C) had no definite melting point and it was difficult to convert them into crystalline derivatives.

When protocatechualdehyde or veratraldehyde was condensed with methyl ethyl ketone in equi-molecular quantity in the presence of hydrochloric acid, a bimolecular compound of type (C) was obtained. In the case of p-hydroxybenzaldehyde or anisaldehyde, the condensation product, in the presence of hydrochloric acid, was a unimolecular compound when each molecule of aldehyde and ketone was used, and this was the case even when

(1) *Ber.*, **14** (1881), 350.
(2) *Sci. Rep. Tohoku Imp. Univ.*, **14** (1925), 123.

half the quantity of the latter was used, i.e. a condition which is in favour of bimolecular formation of the compound. It thus follows that the formation of a bimolecular compound is not the effect of the hydroxyl or methoxyl group in para-position to the aldehyde group. On the contrary, it is the effect of the hydroxyl or methoxyl group in meta-position to the aldehyde group. In the support of this view, the substance of type (C) was the sole product of the condensation of methyl ethyl ketone with m-hydroxybenzaldehyde and its ether, in the presence of hydrochloric acid, even when each molecule of aldehyde and ketone, favourable to the formation of a unimolecular compound, was used.

In the presence of dilute alkali, the condensation products of methyl ethyl ketone with various aldehydes were found to be unimolecular compounds.

Experimental.

α-Methyl-3:4:3′:4′-tetramethoxydistyryl Ketone, $(CH_3O)_2C_6H_3CH:C(CH_3)COCH:CHC_6H_3(OCH_3)_2$. A mixture of veratraldehyde (3 gr.), methyl ethyl ketone (1.5 gr.) and concentrated hydrochloric acid (d = 1.19; 6 c.c.) was allowed to stand for 6 days, and the black, violet product was ground in dilute alkali, collected, washed with water and dried. It was dissolved in benzene, boiled with the addition of animal charcoal, and after being filtered, precipitated with petroleum ether. On repeating this process, a dark, yellow, amorphous powder was obtained (Found: C = 71.77; H = 6.31. $C_{22}H_{24}O_5$ requires C = 71.70; H = 6.57%).

When half the above quantity of the ketone was used, the result was the same.

α-Methyl-3:4:3′:4′-tetrahydroxydistyryl Ketone, $(OH)_2C_6H_3CH:C(CH_3)CO CH:CHC_6H_3(OH)_2$. To an ice-cooled mixture of protocatechualdehyde (2 gr.; 1 mol.) and methyl ethyl ketone (1 gr.; 1 mol.), concentrated hydrochloric acid (d = 1.19; 5 c.c.) was added. After standing for 6 days, the black mass was ground, collected and washed with water. It was dissolved in glacial acetic acid and precipitated with water. On repeating this operation, it separated as a black, violet powder, which, after being dried at 90–100° under reduced pressure, was analysed (Found: C = 69.14; H = 5.13. $C_{18}H_{16}O_5$ requires C = 69.20; H = 5.16%). On heating, this substance carbonises without melting.

The same result was obtained by using ½ mol. of the ketone and 1 mol. of the aldehyde.

The Methyl Ether, $(CH_3O)_2C_6H_3CH:C(CH_3)COCH:CHC_6H_3(OCH_3)_2$. α-Methyl-3:4:3′:4′-tetrahydroxydistyryl ketone was methylated with methyl sulphate and alkali. After being purified by dissolving it in benzene and

precipitating it with petroleum ether, a brown, amorphous substance was obtained (Found : C=71.44 ; H=6.28. $C_{22}H_{24}O_5$ requires C=71.70 ; C=6.57%).

α-Methyl-p-methoxystyryl Methyl Ketone, $(CH_3O)C_6H_4CH:C(CH_3)COCH_3$. A mixture of anisaldehyde (27 gr.) and methyl ethyl ketone (15 gr.) was cooled in ice-water, saturated with dry hydrogen chloride, and allowed to stand overnight. The dark, green product was made alkaline and extracted with ether, washed with water and dried. After the removal of the ether, the residual oil was fractionated under a reduced pressure of 12 mm., when a faint, yellow oil (26 gr.) boiling at 278–281° passed over, which, on cooling, solidified to yellow crystals. These were recrystallised from a mixture of ether and petroleum ether with the addition of animal charcoal, when they separated in colourless crystals, m.p. 27.5–28° (Found : C=75.62 ; H=7.26. $C_{12}H_{14}O_2$ requires C=75.76 ; H=7.42%).

When concentrated hydrochloric acid was used instead of dry hydrogen chloride, the result was almost the same, but the yield was poor. When the quantity of the aldehyde was doubled in the above case, nothing definite could be isolated.

The Oxime, $(CH_3O)C_6H_4CH:C(CH_3)C(:NOH)CH_3$. A solution of the ketone (2 gr.), hydroxylamine hydrochloride (0.8 gr.) and sodium acetate (1.6 gr.) in dilute alcohol was boiled for 1½ hours under a reflux condenser. On recrystallising the crude product from alcohol, colourless needles, m.p. 126,5–128°, were obtained (Found : N=6.88. $C_{12}H_{15}O_2N$ requires N=6.83%).

The Dibromide, $(CH_3O)C_6H_4CHBrC(CH_3)BrCOCH_3$. To a chloroform solution of the ketone, a solution of bromine in the same solvent was added drop by drop, and allowed to stand for 10 minutes. The chloroform was removed under diminished pressure without the application of heat, and the residue was recrystallised from a mixture of ether and petroleum ether, when it separated in colourless crystals, m.p. 70.5–71°, which decomposed gradually (Found : Br=45.57. $C_{12}H_{14}O_2Br_2$ requires Br=45.67%).

Action of Sodium Hypochlorite. To a freshly prepared solution of sodium hypochlorite from bleaching powder and sodium carbonate, the ketone was added and warmed until the evolution of chloroform had ceased. The solution was acidified with dilute sulphuric acid and the precipitate was recrystallised from dilute alcohol, from which it separated in colourless crystals, m.p. 154.5–155° (Found : C=68.73 ; H=6.37. $C_{11}H_{12}O_3$ requires C=68.71 ; H=6.30%).

Perkin[1] gave 154° as its melting point.

p-Methoxystyryl Ethyl Ketone, $(CH_3O)C_6H_4CH:CHCOC_2H_5$. To a mixture of 50 c.c. of water and 20 gr. of a 10% solution of sodium hydroxide, 2

(1) *J. Chem. Soc.*, 31 (1877), 411.

gr. of anisaldehyde and 1.1 gr. of methyl ethyl ketone were added. After shaking the whole for 2 days, the yellow crystals which separated were collected, washed with water and dried. Colourless scales, m.p. 58.5–59°, were obtained after recrystallisation from a mixture of ether and petroleum ether (Found : C = 75.87 ; H = 7.48. $C_{12}H_{14}O_2$ requires C = 75.76 ; H = 7.42%).

Ryan and Cahill[1] gave 53° as its melting point.

The Oxime, $(CH_3O)C_6H_4CH{:}CHC(:NOH)C_2H_5$. This was prepared in the same way as α-methyl-p-methoxystyryl methyl ketoxime. It crystallised in colourless needles, m.p. 138–139°, from alcohol (Found : N = 7.00. $C_{12}H_{15}O_2N$ requires N = 6.83%).

The Dibromide, $(CH_3O)C_6H_4CHBrCHBrCOC_2H_5$. This compound was also synthesised in the same manner as its isomer. It is colourless crystals which decompose at 87.5° (Found : Br = 45.58. $C_{12}H_{14}O_2Br_2$ requires Br = 45.67%).

Ryan and Cahill described 85° as its melting point.

α-Methyl-p-hydroxystyryl Methyl Ketone, $(OH)C_6H_4CH{:}C(CH_3)COCH_3$. A well-cooled mixture of p-hydroxybenzaldehyde (5 gr.) and methyl ethyl ketone (3 gr.) was saturated with dry hydrogen chloride, when a green mass was obtained. After standing overnight, it was dissolved in dilute alkali solution, filtered, and acidified with dilute hydrochloric acid. The grey crystals which were deposited were collected and recrystallised from dilute alcohol with the addition of animal charcoal, when they separated in yellow crystals, m.p. 108.5–109.5° (Found : C = 74.96 ; H = 6.87. $C_{11}H_{12}O_2$ requires C = 74.79 ; H = 7.17%).

The condensation product was the same as that described above, when the condensation was effected with concentrated hydrochloric acid or when half the quantity of the ketone was used.

The Oxime, $(OH)C_6H_4CH{:}C(CH_3)C(:NOH)CH_3$. This was prepared in the same manner as α-methyl-p-methoxystyryl methyl ketoxime. The oxime was colourless and melted at 147–148° (Found : N = 7.39. $C_{11}H_{13}O_2N$ requires N = 7.33%).

The Benzoyl Derivative, $(C_6H_5COO)C_6H_4CH{:}C(CH_3)COCH_3$. α-Methyl-p-hydroxystyryl methyl ketone was benzoylated by Schotten-Baumann's method and the raw product was recrystallised from dilute alcohol, from which it separated in colourless crystals, m.p. 124–125° (Found : C = 77.26 ; H = 6.02. $C_{18}H_{16}O_3$ requires C = 77.11 ; H = 5.76%).

The Methyl Ether, $(CH_3O)C_6H_4CH{:}C(CH_3)COCH_3$. α-Methyl-p-hydroxystyryl methyl ketone was methylated with methyl iodide and alcoholic potash and the crude product was recrystallised from a mixture of ether and

(1) *J. Chem. Soc.*, **128** (1925), 1, 558.

petroleum ether, when it crystallised in colourless crystals, m.p. 27.5–28.5°. The melting point was not changed by admixture with α-methyl-p-methoxystyryl methyl ketone obtained by the condensation of anisaldehyde with methyl ethyl ketone.

α-Methyl-m : m′-dimethoxydistyryl Ketone, $(CH_3O)C_6H_4CH:C(CH_3)COCH:CHC_6H_4(OCH_3)$. An ice-cooled mixture of m-hydroxybenzaldehyde (1 gr.; 1 mol.) and methyl ethyl ketone (0.55 gr.; 1 mol.) was saturated with dry hydrogen chloride when a deep, scarlet, viscid oil was obtained. After being allowed to remain overnight, it was extracted with ether, washed with water and dried. The ether was removed and the residue was dissolved in benzene and precipitated with petroleum ether. On repeating this operation, a small quantity of yellow, amorphous substance was obtained, which, after being dried at 80–90° under reduced pressure, was analysed (Found : C = 77.78 ; H = 6.98. $C_{20}H_{20}O_3$ requires C = 77.88 ; H = 6.54%).

The same substance was obtained by condensing 1 mol. of the aldehyde with ½ mol. of the ketone.

α-Methyl-m : m′-dihydroxydistyryl Ketone, $(OH)C_6H_4CH:C(CH_3)COCH:CHC_6H_4(OH)$. To a mixture of m-hydroxybenzaldehyde (2 gr.) and methyl ethyl ketone (1.2 gr.), cooled in ice-water, 5 c.c. of concentrated hydrochloric acid (d = 1.19) was added and left for 6 days. The dark, brown mass thus obtained was treated similarly as in the case of the condensation product of protocatechualdehyde with methyl ethyl ketone, when a brick-red powder was obtained which was analysed after being dried at 80–90° for an hour under reduced pressure (Found : C = 77.25 ; H = 5.86. $C_{18}H_{16}O_3$ requires C = 77.11 ; H = 5.76%).

The product was the same on condensing half the quantity of the ketone with the aldehyde.

The Methyl Ether, $(CH_3O)C_6H_4CH:C(CH_3)COCH:CHC_6H_4(OCH_3)$. This substance was prepared by shaking the ketone with methyl sulphate and alkali, and purified by precipitating it from the benzene solution with petroleum ether as described in the case of α-methyl-3:4:3′:4′-tetramethoxydistyryl ketone, when it separated as a dark, yellow powder, which was analysed after being dried at 90-100° under reduced pressure (Found : C = 78.16 ; H = 6.25. $C_{20}H_{20}O_3$ requires C = 77.88 ; H = 6.54%).

3:4-Methylendioxystyryl Ethyl Ketone, $CH_2O_2C_6H_3CH:CHCOC_2H_5$. To a mixture of 100 c.c. of water and 20 c.c. of a 10% sodium hydroxide solution, 5 gr. of piperonal and 2.5 gr. of methyl ethyl ketone were added and allowed to stand for 2 days, when yellow crystals were separated. On recrystallising from dilute alcohol, they separated in yellow crystals, m.p. 101.5–102° (Found : C = 70.73 ; H = 5.99. $C_{12}H_{12}O_3$ requires C = 70.55 ; H = 5.93%).

Ryan and Cahill gave 101–102° as its melting point.

The Oxime, $CH_2O_2C_6H_3CH{:}CHC(:NOH)C_2H_5$. This was prepared by the same method as in the synthesis of p-methoxystyryl ethyl ketoxime. The crude product was recrystallised from alcohol in faint, yellow crystals, m.p. 173° (decomp.) (Found : N = 6.50 ; $C_{12}H_{13}O_3N$ requires N = 6.39%).

The Dibromide, $CH_2O_2C_6H_3CHBrCHBrCOC_2H_5$. This was synthesised by the same method as in the case of p-methoxystyryl ethyl ketone dibromide. It crystallised in colourless crystals, m.p. 93.5–94°, from a mixture of ether and petroleum ether (Found : Br = 43.94. $C_{12}H_{12}O_3Br_2$ requires Br = 43.92%).

In conclusion, the author wishes to express his hearty thanks to Professor Hiroshi Nomura under whose guidance this investigation was carried out.

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THE OCCURRENCE OF FREE PENTOSE IN BAMBOO SHOOTS. (STUDIES ON JAPANESE PLANTS. VIII.)[1]

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On the occurrence of free pentoses in plants, the evidence was offered by Davis and Sawyer,[2] as suggested by the work of de Chalmot,[3] from the Kröber-Tollens determination of pentoses in the extract of some vegetables, prepared with ammoniacal alcohol, and the contribution which supports this view was reported by A. G. Spoehr,[4] studying the carbohydrate economy of cacti. However, the treatment of the plant materials, employed by Davis and his co-workers, and Spoehr, as these were pointed out by D. T. Englis and C. Hale,[5] would then throw some doubt as to the conclusiveness of the evidence, owing to the fact that the desiccation of plant materials at high temperature,[6] and the use of ammonia and other weak alkalis for the extraction of sugars, could have given rise to a product which would lead to the

(1) The articles I, II, III, IV, V, and VII have been published in *The Mem. Coll. Sci. Kyoto Imp. Univ.*, **6** (1923), 295; **7** (1923), 7; **9** (1925), 1; **8** (1925), 59; 223; 253.
(2) *J. Agr. Sci.*, **6** (1914), 406.
(3) *Am. Chem. J.*, **15** (1893), 21; **16** (1894), 16; *J. Am. Chem. Soc.*, **15** (1893), 618.
(4) "The Carbohydrate Economy of Cacti," (1919), p. 41.
(5) *J. Am. Chem. Soc.*, **47** (1925), 446.
(6) K. P. Link, ibid., **47** (1925), 470 and refer W. Stiles, "Photosynthesis," (1925), p. 145.

formation of furfural-like compounds by some intramolecular changes or some degradation of hexoses.

In view of these facts, it appears that the only reliable method for the evidence of the occurrence of free pentoses, must be based upon the isolation of these sugars of the expressed juice which was prepared on the spot where the plant materials were freshly gathered.

In the phytochemical study of bamboo shoots, one of the writers (S. K.) and Ch. Tanaka[1] have reported that the pentose-content, which was determined by Kröber-Tollens' method, was constant throughout the bamboo shoot life, and the conviction of the occurrence of pentose in the free state came to the writers from a consideration of the origin of the sugars in plant tissues, ascribing them to the metabolism of hexoses, but not to the photosynthesis of carbon dioxide. The endeavours by which free pentose was isolated, will open the way for some suggestion as to the provenance of pentoses in nature.

The material used in this experiment was the shoots of the Madake (*Phyllostachys quilioli, F. M.*), which were obtained from a bamboo grove in Yamanouchi, Kyoto, located two miles from the laboratory. The shoots were minced in a mincing machine within an hour of gathering, and the minced mass was pressed by means of a hydraulic press. The juice thus obtained was poured into absolute alcohol. The manipulation was carried out as rapidly as possible in order to avoid all danger from enzyme actions on the carbohydrates.

13 Kg. of shoots yielded 10 litres of the expressed-juice of a density of 1.02; and this juice contained 160 gr. of reducing sugar calculated to be d-glucose from its power of reducing Fehling's solution.

To the juice a sufficient quantity of alcohol (30 litres) was added, whereon a voluminous precipitate was formed, which was filtered, washed well with alcohol and the filtrate subjected to distillation under reduced pressure to distill off the alcohol, and then diluted with water. To get sugars only, a slight excess of basic lead acetate was added to precipitate glucuronic acid with some organic acids which occur in the juice and the precipitate was filtered off, the excess of lead was removed by hydrogen sulphide gas. The colourless solution was evaporated to syrup under reduced pressure and the reducing sugars were extracted with absolute alcohol, evaporated again to a thick syrup and treated with alcohol. The operation was repeated three times, and the final extract containing 111.68 gr. of d-glucose and 12.88 gr. of l-xylose calculated from the reducing power of Fehling's solution and from the quantity of furfural measured by Kröber-Tollens' method, was evaporated under reduced pressure to a thick syrup. After clarifying with basic lead

(1) Loc. cit.

acetate, and an equal volume of glacial acetic acid was added to the syrup to crystallize the d-glucose, and actually 43 gr. of d-glucose. m.p. 145°, were isolated in a white crystalline state. The filtrate from the crystallized d-glucose, containing 49.5 gr. of reducing sugar, was diluted with water, and the acetic acid was expelled by distillation under reduced pressure, and the solution concentrated to 200 c.c.; it gave a polarization of $\alpha_D = 26°.9$ in a 1 dm. tube. Half of the sugar solution was diluted with water to make approximately a 10% aqueous solution, and about 5 gr. of top yeast were added, together with about 5 gr. of malt sprouts as a nitrogenous yeast food in order to ferment some hexoses remained in the solution with pentose. Fermentation proceeded at room temperature. After four days from the start, the fermentation had ceased and the solution was then cleared with a slight excess of basic lead acetate, the precipitate filtered, the excess of lead in the filtrate was precipitated by hydrogen sulphide gas, decolorized with active carbon and the solution again filtered. The solution freed from hydrogen sulphide, showed a polarization of $\alpha_D = 19°.2$ in a 1 dm. tube, contained 6.11 gr. and 6.13 gr. of l-xylose calculated from the reducing power of Fehling's solution, and the furfural-content by the Kröber-Tollens' method respectively. As concentrating the solution under reduced pressure, sugar was crystallized and the yield of the crude material was 5.4 gr. The sugar purified from its aqueous solution, melted at 145–150°, and showed a dextro-rotation in aqueous solution,

$$[\alpha]_D^{18} = \frac{0.39 \times 100}{2 \times 1.015} = +19°.21$$

Analysis, (C=39.95; H=6.65), indicated that the sugar has the formula $C_5H_{10}O_5$ (it requires, C=40.00; H=6.66%). For confirmation to be l-xylose, it was transformed into l-xylose osazone, m.p. 159°, and into xylonic acid by oxidation with bromine, and the latter was identified as the double salt of cadmium bromide with cadmium xylonate, following the method suggested by G. Bertrand.(1) It gave on analysis, Br=20.78; while theory requires Br=21.32 for $(C_5H_9O_6)_2Cd \cdot CdBr_2 \cdot 2H_2O$.

The isolation of l-xylose in a crystalline state from the pressed juice of bamboo shoots was successful, and this is probably the first example that pentose has been obtained direct in crystalline form from vegetable tissues.

Moreover, it is noteworthy fact that glucuronic acid which was regarded as an intermediate product of glucose metabolism in nature, was isolated from the precipitate by basic lead acetate mentioned above. For the recognition of glucuronic acid,(2) the precipitate which formed by basic lead acetate, suspended in water was decomposed by means of hydrogen sulphide gas, and

(1) *Bull. soc. chim.*, [3] **5** (1891), 556.

(2) Refer C. G. Schwalbe and G. A. Feldtmann, *Ber.*, **58** (1925), 1535.

the free acid in solution was isolated by converting it into barium salt of the phenylosazone[1] (m.p. 192°). The analytical results of the barium salt, $C_{36}H_{38}O_{10}N_8Ba$, are : C = 48.98 ; H = 4.76 ; N = 12.68%.

The discovery of these substances in such a vigorously growing part of the plant, should account for much of formation of pentoses by the metabolic changes of hexoses in plants.

In addition, pectinic substance was isolated in an impure state from the pressed juice of the shoots, which yields pentose by hydrolysis and mucic acid by oxidation.

In fact, pectines and mucilages,[2] their basal molecule consists of xylose, glucose and glucuronic acid or arabinose, galactose and galacturonic acid, have been very generally occured in nature with the pentoses and hexoses. These facts strongly support the hypothesis of pentose formation above mentioned.

In conclusion, the writers desire to express their thanks to Mr. N. Iguchi for furnishing valuable materials used in this investigation.

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(1) Goldschmidt, *Monatsh.*, **31** (1910), 477.

(2) F. Ehrlich, *Chem. Ztg.*, **44** (1917), 197; T. von Fellenberg, *Biochem. Z.*, **85** (1918), 82; W. H. Dore, *J. Ind. & Eng. Chem.*, **16** (1924), 1042; S. Komatsu and H. Ueda, *The Mem. Coll. Sci. Kyoto Imp. Univ.*, A, **8** (1925), 51; D. R. Nanji, F. I. Paton and A. R. Ling *J. Soc. Chem. Ind.*, **44** (1925), 253; J. W. Mikinney, *J. Soc. Chem. Ind.*, **45** (1926), 301.